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(54) **FORMATION OF TITANIUM ANODICALLY OXIDIZED FILM FOR PHOTOCATALYST**

(57)Abstract:

PROBLEM TO BE SOLVED: To allow a film to exhibit photocatalytic operation even by ultraviolet rays and visible rays and to obtain antibacterial, deodorant and contamination preventive effects by immersing titanium into an electrolytic bath composed of sulfuric acid, phosphoric acid and hydrogen peroxide, increasing the voltage to the prescribed one by a prescribed direct constant current and holding it for a prescribed time to form a titanium anodically oxidized film essentially consisting of an anatase form.

SOLUTION: This is a method for forming a titanium anodically oxidized film for a photocatalyst exhibiting photocatalytic operation even by visible rays, in which titanium is immersed into an electrolytic bath composed of sulfuric acid, phosphoric acid, hydrogen peroxide and cobalt sulfate, the voltage is increased to the prescribed one by a prescribed direct constant current, and it is held for a prescribed time to form a TiO<sub>2</sub>-CoO series titanium anodically oxidized film. Moreover, titanium is immersed into an electrolytic bath composed of sulfuric acid, phosphoric acid, hydrogen peroxide and zinc sulfate, the voltage is increased to the prescribed one, and it is held for a prescribed time to form a TiO<sub>2</sub>-ZnO series titanium anodically oxidized film. The titanium anodically oxidized film to be formed is used for the interior and exterior materials of buildings, apparatus for cooking, tableware or the like.

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CLAIMS

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## [Claim(s)]

[Claim 1] The generation method of the titanium anodic oxide film including the coat generation main process which is the generation method of the titanium anodic oxide film for photocatalysts which demonstrates a photocatalyst operation also by the visible ray, and consists of a process which generates the anodic oxide film of the titanium which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, and a hydrogen peroxide, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined-time maintenance on that electrical potential difference after a pressure up, and makes an ANATASU form a subject for photocatalysts.

[Claim 2] The generation method of the titanium anodic oxidation coatings including the coat generation main process which is the generation method of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation also by the visible ray, and consists of a process which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and cobalt sulfate, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined-time maintenance on that electrical potential difference after a pressure up, and generates the anodic oxidation coatings of the titanium of a TiO<sub>2</sub>-CoO system for photocatalysts.

[Claim 3] The generation method of the titanium anodic oxide film including the coat generation main process which is the generation method of the titanium anodic oxide film for photocatalysts which demonstrates a photocatalyst operation also by the visible ray, and consists of a process which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and a zinc sulfate, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined-time maintenance on that electrical potential difference after a pressure up, and generates the anodic oxide film of the titanium of a TiO<sub>2</sub>-ZnO system for photocatalysts.

[Claim 4] The generation method of the titanium anodic oxide film including the coat generation main process which is the generation method of the titanium anodic oxide film for photocatalysts which demonstrates a photocatalyst operation also by the visible ray, and consists of a process which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and a sulfuric-acid ruthenium, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined-time maintenance on that electrical potential difference after a pressure up, and generates the anodic oxide film of the titanium of TiO<sub>2</sub>-RuO<sub>2</sub> system for photocatalysts.

[Claim 5] The generation method of the titanium anodic oxidation coatings including the coat generation main process which is the generation method of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation also by the visible ray, and consists of a process which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, and a zinc sulfate, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined time maintenance on that electrical potential difference after a pressure up, and generates the anodic oxidation coatings of the titanium of a TiO<sub>2</sub>-

CoO-ZnO system for photocatalysts.

[Claim 6] Also by the visible ray, are the generation method of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation, and prepare the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, and a sulfuric-acid ruthenium, and titanium is immersed in this electrolytic bath. The generation method of the titanium anodic oxidation coatings for photocatalysts including the coat generation main process which consists of a process which carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined time maintenance on the electrical potential difference after a pressure up, and generates the anodic oxidation coatings of the titanium of TiO<sub>2</sub>-CoO-RuO<sub>2</sub> system.

[Claim 7] Also by the visible ray, are the generation method of the titanium anodic oxide film for photocatalysts which demonstrates a photocatalyst operation, and prepare the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, a zinc sulfate, and a sulfuric-acid ruthenium, and titanium is immersed in this electrolytic bath. The generation method of the titanium anodic oxidation coatings for photocatalysts including the coat generation main process which consists of a process which carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined time maintenance on the electrical potential difference after a pressure up, and generates the anodic oxidation coatings of the titanium of TiO<sub>2</sub>-ZnO-RuO<sub>2</sub> system.

[Claim 8] Also by the visible ray, are the generation method of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation, and prepare the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, a zinc sulfate, and a sulfuric-acid ruthenium, and titanium is immersed in this electrolytic bath. The generation method of the titanium anodic oxidation coatings for photocatalysts including the coat generation main process which consists of a process which carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined time maintenance on the electrical potential difference after a pressure up, and generates the anodic oxidation coatings of the titanium of TiO<sub>2</sub>-CoO-ZnO-RuO<sub>2</sub> system.

[Claim 9] The generation method of the titanium anodic oxide film for photocatalysts which includes the removal process in which the sulfuric acid and phosphoric-acid ion in an anodic oxide film are removed by replacing an anode plate and cathode and electrolyzing by changing an electrical potential difference, in the generation method of the titanium anodic oxide film for photocatalysts according to claim 1 to 8 after said coat generation main process generates an anodic oxide film.

[Claim 10] The generation method of the titanium anodic oxide film for photocatalysts which adds ammonium fluoride in an electrolytic bath and generates the anodic oxide film of the titanium of fluorine content in said coat generation main process in the generation method of the titanium anodic oxide film for photocatalysts according to claim 1 to 8.

[Claim 11] The generation method of the titanium anodic oxidation coatings for photocatalysts including the colloid deposit process in which the titanium by which anodizing was carried out in said coat generation main process is immersed into the water solution of the chloride of noble metals in the generation method of the titanium anodic oxidation coatings for photocatalysts according to claim 1 to 8, perform UV irradiation, and the reduction deposit of the colloid of noble metals is carried out on the surface of anodic oxidation coatings.

[Claim 12] The generation method of the titanium anodic oxidation coatings for photocatalysts which are the generation methods of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation also by the visible ray, and add the fluorine of a minute amount in a coat while removing low hypo---ic acid-ized titanium from these anodic oxidation coatings, after primary anodization generates anodic oxidation coatings to titanium.

[Claim 13] The generation method of the titanium anodic oxidation coatings for photocatalysts which are immersed in the electrolytic bath which is the generation method of the titanium anodic oxidation coatings for photocatalysts which demonstrate a photocatalyst operation also by the visible ray, and contains fluoride ion, such as ammonium hydrogendifluoride, fluoric acid, or ammonium fluoride, for the titanium with which this coat was generated after primary anodization generates anodic oxidation coatings to titanium, or the electrolytic bath which contains a hydrogen peroxide in this, and perform re-

anodization.

[Claim 14] The anodic oxidation coatings formed by primary anodization are the generation methods of the titanium anodic oxidation coatings for photocatalysts according to claim 12 or 13 which are the thick-film form anodic oxidation coatings which use an anatase type titanium dioxide as a principal component.

[Claim 15] The anodic oxide film formed by primary anodic oxidation is the generation method of the titanium anodic oxide film for photocatalysts according to claim 12 or 13 which is a coat formed in the coat generation main process in either claim 1 thru/or claim 8 and the generation method of the titanium anodic oxide film for photocatalysts according to claim 10.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] this invention -- the inside of various building materials, other devices, and an ingredient, for example, a building, a sheathing material, and cooking -- an appliance -- it is related with the generation method of the titanium anodic oxide film for photocatalysts used for charges of engineering-works material, such as an implement, a tableware, a health device, and other sewer pipes, etc.

**[0002]**

[Description of the Prior Art] Corrosion resistance of titanium is the strongest among a practical use metal, its specific gravity is also small as compared with steel etc., and specific strength is also a very excellent metal and is widely used for the construction materials for works plants, a medical-application ingredient, etc. And use to building materials including roofing is progressing quickly with the high corrosion resistance in recent years. Moreover, self-purification by the photocatalyst operation which was discovered in the 1970s and which titanium oxide has, air cleaning, and a germicidal action are capturing the spotlight with actualization of an environmental problem in recent years, and the research turned to utilization also in the structural ingredient field is progressing. That is, if the ultraviolet rays from sunlight, lighting fitting, etc. are irradiated at titanium oxide, light energy will be transformed into chemical energy, the photocatalyst operation which disassembles the organic substance etc. will be demonstrated, and antibacterial, deodorization, and the antifouling effectiveness other than decomposition removal of the formaldehyde which is the typical allergen generated in office and the housing interior of a room will be acquired.

**[0003]**

[Problem(s) to be Solved by the Invention] However, the photocatalyst operation by conventional titanium oxide is demonstrated only by irradiating ultraviolet rays. However, since there are very few amounts of the ultraviolet rays included in sunlight, lighting fitting, etc., sufficient effectiveness may not be acquired and the application is also restricted.

[0004] Then, this invention aims at offering the generation method of the titanium anodic oxide film for photocatalysts with which a photocatalyst operation is demonstrated not only by ultraviolet rays but by the visible ray, and antibacterial [ outstanding ], deodorization, and the antifouling effectiveness are acquired.

**[0005]**

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the generation method of the titanium anodic oxide film for photocatalysts concerning the 1st invention according to claim 1 generates the anodic oxide film of the titanium which prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, and a hydrogen peroxide as a coat generation main process, is immersed in this electrolytic bath in titanium, carries out a pressure up even to a predetermined electrical potential difference by predetermined direct-current constant current, carries out predetermined time maintenance on that electrical potential difference after a pressure up, and makes an ANATASU form a subject. ANATASU, BURUKKAITO, and three kinds of crystal form of a rutile existing in titanium oxide, and having photocatalyst activity with the most expensive ANATASU crystal in it is the fact known well.

[0006] The generation method concerning the 2nd invention according to claim 2 prepares the

electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and cobalt sulfate as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of a TiO<sub>2</sub>-CoO system.

[0007] The generation method concerning the 3rd invention according to claim 3 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and a zinc sulfate as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of a TiO<sub>2</sub>-ZnO system.

[0008] The generation method concerning the 4th invention according to claim 4 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, and a sulfuric-acid ruthenium as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of TiO<sub>2</sub>-RuO<sub>2</sub> system.

[0009] The generation method concerning the 5th invention according to claim 5 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, and a zinc sulfate as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of a TiO<sub>2</sub>-CoO-ZnO system.

[0010] The generation method concerning the 6th invention according to claim 6 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, and a sulfuric-acid ruthenium as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of TiO<sub>2</sub>-CoO-RuO<sub>2</sub> system.

[0011] The generation method concerning the 7th invention according to claim 7 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, a zinc sulfate, and a sulfuric-acid ruthenium as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of TiO<sub>2</sub>-ZnO-RuO<sub>2</sub> system.

[0012] The generation method concerning the 8th invention according to claim 8 prepares the electrolytic bath which consists of a sulfuric acid, a phosphoric acid, a hydrogen peroxide, cobalt sulfate, a zinc sulfate, and a sulfuric-acid ruthenium as a coat generation main process, performs the same electrolysis processing as the case of the 1st invention using this electrolytic bath, and generates the anodic oxide film of the titanium of TiO<sub>2</sub>-CoO-ZnO-RuO<sub>2</sub> system.

[0013] If the anodic oxide film of the titanium generated in the above coat generation main process of the 1st - the 8th invention performs predetermined processing, a photocatalyst operation will be demonstrated not only by ultraviolet rays but by the visible ray, and antibacterial [ outstanding ], deodorization, and the antifouling effectiveness will be acquired. therefore -- application expansion of said titanium anodic oxide film is possible -- becoming -- the inside of a building, a sheathing material, and cooking -- an appliance -- use optimal as charges of engineering-works material, such as an implement, a tableware, a health device, and other sewer pipes, etc. can be performed.

[0014] With the desirable operation gestalt (the 1 another operation gestalt) of each [ these ] invention, after generating an anodic oxide film in the coat generation main process of each above-mentioned invention, the removal process in which the sulfuric acid and phosphoric-acid ion in an anodic oxide film are removed is included by replacing an anode plate and cathode and electrolyzing by changing an electrical potential difference. Thus, if the sulfuric acid and phosphoric-acid ion in an anodic oxide film are removed, the corrosion resistance of a coat will increase and the use optimal as a sheathing material of a building etc. will be attained. And a photocatalyst operation of a titanium anodic oxide film is raised by removal of these impurity ion that works as a charge carrier's recombination center generated in titanium oxide by light absorption, and antibacterial [ outstanding ], deodorization, and the antifouling effectiveness are acquired by it.

[0015] Moreover, with a desirable operation gestalt (the 2 another operation gestalt), ammonium fluoride is added in the electrolytic bath used by each above-mentioned invention, and the anodic oxide film of the titanium of fluorine content is generated. If it does in this way, since a fluorine or a fluorine

compound will be formed in the front face of a titanium anodic oxide film, the reinforcement of a coat will be strengthened and the weatherability of a coat will improve, the optimal use as a sheathing material etc. is attained among buildings. And a photocatalyst operation of a titanium anodic oxide film is raised further, and antibacterial [ further excellent ], deodorization, and the antifouling effectiveness are acquired. Although it now is not clear about the cause of the photocatalyst operation promotion effectiveness of fluorine ion, it is related to promoting ANATASU crystallization, and needs.

[0016] Furthermore, with a desirable operation gestalt (the 3 another operation gestalt), the titanium by which anodizing was carried out in the coat generation main process of each above-mentioned invention is immersed into the water solution of the chloride of noble metals, UV irradiation is performed, and the colloid deposit process in which the reduction deposit of the colloid of noble metals is carried out on the surface of an anodic oxide film is included. If it does in this way, since the noble metals which deposited on the front face of a titanium anodic oxide film will demonstrate a good photocatalyst operation, antibacterial [ further excellent ], deodorization, and the antifouling effectiveness are acquired. An optical charge carrier's charge separation will be raised by support of noble metals, and it will be effectively used for oxidation / reduction reaction of the organic substance. The organic substance decomposition removal function of titanium oxide originates in the strong oxidizing power of the electron hole generated to a valence band by optical pumping. RuO<sub>2</sub> Since migration to the organic substance of an electron hole is helped, it is effective in especially making the oxidation effectiveness of the organic substance increase.

[0017] The generation method of the titanium anodic oxidation coatings for photocatalysts concerning the 9th invention according to claim 12 is the approach of adding the fluorine of a minute amount in a coat while removing low hypo---ic acid-ized titanium from these anodic oxidation coatings, after generating anodic oxidation coatings by primary anodization to titanium. The approach of adding in a coat can specifically perform the fluorine of a minute amount by the approach of the 10th following invention by removing low hypo---ic acid-ized titanium. The generation method of the titanium anodic oxidation coatings for photocatalysts concerning the 10th invention according to claim 13 is an approach of it being immersed in the electrolytic bath which contains fluoride ion, such as ammonium hydrogendifluoride, fluoric acid, or ammonium fluoride, for the titanium with which this coat was generated, or the electrolytic bath which contains a hydrogen peroxide in this, and performing re-anodization, after generating anodic oxidation coatings by primary anodization to titanium. If titanium metal is processed by the high voltage during a phosphoric-acid-sulfuric-acid-hydrogen-peroxide-solution bath, the thick-film form anodic oxide film which uses an anatase type titanium dioxide as a principal component will be obtained. However, although this coat is using the anatase type titanium dioxide as the principal component, the way things stand, photocatalyst activity is not shown. This cause is considered based on the low hypo---ic acid-ized titanium which exists in a coat. Then, we decided to remove this. Moreover, re-anodic oxidation of the above-mentioned coat was considered as the approach of this removal. Since it is necessary to dissolve low hypo---ic acid-ized titanium as a bath used for this re-anodization, F ion shall be included. The experiment showed that photocatalyst activity could be given to an anodic oxide film by anodizing by the ammonium-hydrogendifluoride bath as secondary treatment. It is considered effective in removing the low hypo---ic acid-ized titanium in a coat, and coincidence by this to dope a fluorine in a coat. The sample of this of an immersion experiment is clearer than catalytic activity was not shown but the sample by secondary anodic oxidation showed catalytic activity. That is, at the time of secondary anodization, the fluorine ion of the ammonium hydrogendifluoride used for low hypo---ic acid-ized titanium removal enters into a titanium oxide coat by electrophoresis, and builds impurity level, and it is possible that photocatalyst activity improved as a result etc.

[0018] In these 9th invention and the 10th invention, the anodic oxidation coatings formed by primary anodization may be thick-film form anodic oxidation coatings which use an anatase type titanium dioxide as a principal component.

[0019] Moreover, in the 9th above-mentioned invention, the anodic oxide film formed by primary anodic oxidation may be a coat formed in the coat generation main process in the above 1st thru/or the 8th one of invention, or the generation method of the titanium anodic oxide film for photocatalysts in the above-mentioned 2nd exception operation gestalt. That is, the coat formed in the coat generation main process under each above-mentioned invention is used as a middle generation article. Furthermore, in



the 10th above-mentioned invention, the anodic oxidation coatings formed by primary anodic oxidation may be coats formed in the coat generation main process in the generation method of the titanium anodic oxidation coatings for photocatalysts in the above 1st thru/or the 8th one of invention. In addition, in the 9th above-mentioned invention and the 10th invention, the anodic oxide film formed by primary anodic oxidation may be a coat after the removal process of the above-mentioned 1st exception operation gestalt, or a coat after the colloid deposit process of the above-mentioned 3rd exception operation gestalt.

[0020]

[Embodiment of the Invention] Hereafter, a concrete example is given and this invention is explained. an example 1 -- the electrolytic bath (a "basic bath" is called hereafter) which consists of the sulfuric acid ( $\text{H}_2\text{SO}_4$ ) of 1.5 mol/L (L is a liter in addition), a phosphoric acid ( $\text{H}_3\text{PO}_4$ ) of 0.3 mol/L, and hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ ) of 0.3 mol/L is prepared first. And titanium is immersed into this electrolytic bath, a pressure up is carried out even to 200V by 20 degrees C of bath temperature, and direct-current constant current 1 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film ( $\text{TiO}_2$ ) of a rutile form with the subject.

[0021] During the basic bath which is an electrolytic bath used in the example 2 example 1, 0.02 - 0.1 mol/L of cobalt sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) is added further. And a pressure up is carried out to 150V into the electrolytic bath prepared in this way by 30 degrees C of bath temperature, and direct-current constant current 3 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of the  $\text{TiO}_2$ -CoO system of a rutile form with the subject.

[0022] During the example 3 aforementioned basic bath, 0.02 - 0.3 mol/L of a zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) is added further. And titanium is immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 200V by 25 degrees C of bath temperature, and direct-current constant current 1 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of the  $\text{TiO}_2$ -ZnO system of a rutile form with the subject.

[0023] During the example 4 aforementioned basic bath, 0.01 mols / L of a sulfuric-acid ruthenium ( $\text{Ru}_2(\text{SO}_4)_3$ ) are added further. And titanium is immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 200V by 25 degrees C of bath temperature, and direct-current constant current 1 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of  $\text{TiO}_2$ - $\text{RuO}_2$  system of a rutile form with the subject.

[0024] During the example 5 aforementioned basic bath, 0.02 - 0.1 mol/L of cobalt sulfate and 0.02 - 0.3 mol/L of a zinc sulfate are added. And titanium is immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 150V by 30 degrees C of bath temperature, and direct-current constant current 3 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of the  $\text{TiO}_2$ -CoO-ZnO system of a rutile form with the subject.

[0025] During the example 6 aforementioned basic bath, 0.02 - 0.1 mol/L of cobalt sulfate and 0.01 mol/L of a sulfuric-acid ruthenium are added further. And titanium is immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 150V by 30 degrees C of bath temperature, and direct-current constant current 3 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of  $\text{TiO}_2$ -CoO- $\text{RuO}_2$  system of a rutile form with the subject.

[0026] During the example 7 aforementioned basic bath, 0.02 - 0.3 mol/L of a zinc sulfate and 0.01 mol/L of a sulfuric-acid ruthenium are added further. And titanium is immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 200V by 25 degrees C of bath temperature, and direct-current constant current 1 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of  $\text{TiO}_2$ -ZnO- $\text{RuO}_2$  system of a rutile form with the subject.

[0027] During the example 8 aforementioned basic bath, 0.02 - 0.1 mol/L of cobalt sulfate, 0.02 - 0.3 mol/L of a zinc sulfate, and 0.01 mol/L of a sulfuric-acid ruthenium are added further. And titanium is



immersed into the electrolytic bath prepared in this way, a pressure up is carried out even to 150V by 30 degrees C of bath temperature, and direct-current constant current 3 A/dm<sup>2</sup>, after a pressure up, it holds for 5 minutes on this electrical potential difference, and anodizing is performed. Consequently, the ANATASU form was acquired [ the part ] for the titanium anodic oxide film of TiO<sub>2</sub>-CoO-ZnO-RuO<sub>2</sub> system of a rutile form with the subject. in addition, the crystal form of the anodic oxide film by each above example -- XRD -- it is based on the detection result by law.

[0028] After generating an anodic oxide film in the nine or more-example examples 1-8, the sulfate ion (SO<sub>4</sub><sup>2-</sup>) and the phosphoric-acid ion (PO<sub>4</sub><sup>3-</sup>) in an anodic oxide film were removed by replacing an anode plate and cathode and electrolyzing by changing an electrical potential difference in 100-200V.

[0029] In the electrolytic bath used in the ten or more-example examples 1-8, 0.01 mol/L of ammonium fluoride (NH<sub>4</sub>F) was added, anodizing was performed by the same electrolytic condition as each example, and the anodic oxide film of the titanium of fluorine content was generated.

[0030] The titanium which carried out anodizing in the 11 or more-example examples 1-8 was immersed into the water solution of the chloride of Au, Ag, Pd, and Pt, UV irradiation was performed, and the reduction deposit of the colloid of various noble metals was carried out on the surface of the anodic oxide film.

[0031] The trial about the photocatalyst operation by the above examples 1-11 was performed. However, it turned out that photocatalyst activity with these anodic oxide films sufficient the way things stand is not shown. That is, as mentioned above, if titanium metal is processed by the high voltage during a phosphoric-acid-sulfuric-acid-hydrogen-peroxide-solution bath, the thick-film form anodic oxide film which uses an anatase type titanium dioxide as a principal component will be obtained. However, photocatalyst activity is not shown although this coat is using the anatase type titanium dioxide as the principal component.

[0032] This cause was considered based on the low hypo---ic acid-ized titanium considered to exist in a coat, and re-anodic oxidation (secondary anodic oxidation) of this coat was considered as an approach of removing this. Since it is necessary to dissolve low hypo---ic acid-ized titanium as a bath used for this re-anodization, F ion shall be included.

[0033] an example 12 -- it explains with the example of a comparison about the example which performed this secondary anodic oxidation. The titanium used for the experiment is the piece of a plate of one sort of industrial use semi- titanium specified to JISH4600 (0.4mm in width of face of 30mm, die length of 50mm, thickness), and what was immersed in n-hexane as an object for pretreatment for surface cleaning was used for it. In the example 12, following primary anodic oxidation and secondary anodic oxidation were performed about the titanium which consists of this piece of a plate. In the example of a comparison, the next immersion processing was performed after the same primary anodic oxidation as an example 12.

[0034] (1) For anodic oxidation of primary \*\*\*\*\* , a phosphoric acid (H<sub>3</sub> PO<sub>4</sub>) is /L (in addition) 0.3 mols. As for L, a liter and 1.5 mols (H<sub>2</sub> SO<sub>4</sub>) of sulfuric acids are immersed in titanium into the electrolyte (20-50 degrees C) with which /L and 0.3 mols (H<sub>2</sub> O<sub>2</sub>) of hydrogen peroxides consist of a presentation of /L. A completeness smooth direct current is used and it is 3.0 A/dm<sup>2</sup>. The pressure up was carried out to 200V, and it electrolyzed by holding this electrical potential difference for 30 minutes after the pressure up. This processing is considered as primary anodic oxidation.

(2) Secondary anodic oxidation (example) and immersion processing (example of a comparison)  
In the example 12, it tried to remove the low hypo---ic acid-ized titanium in a coat about the sample produced by primary anodic oxidation by performing anodic oxidation (secondary anodic oxidation) for the second time. In the example of a comparison, it tried to remove the low hypo---ic acid-ized titanium in a coat by being immersed into a hydrogen-peroxide-solution-ammonium-hydrogendifluoride water solution about the sample produced by primary anodic oxidation of the same conditions as the case of an example 12. By the above-mentioned secondary anodic oxidation, the concentration of ammonium hydrogendifluoride was changed by /L, bath temperature changed 0.01-0.3 mols of 20 degrees C - 40 degrees C and electrolysis time amount in 5 - 30 minutes, and optimum conditions were examined. The above-mentioned immersion processing performed concentration of ammonium hydrogendifluoride by /L, and performed 0.01-0.5 mols of 20-50 degrees C and immersion time amount for bath temperature in 5 - 90 minutes.

[0035] [Measurement] Check of crystallization of the coat by X diffraction measurement, SEM image

observation, cross-section analysis of the coat by EPMA, and surface analysis by XPS were performed to the coat of the example 12 created in this way and the example of a comparison.

[0036] [Test result]

(Appearance of a coat) Each sample produced by primary anodic oxidation is gray. Although this has suggested that the titanium dioxide which is the component of the white called into a coat the low hypo--ic acid-ized titanium which is a black component is intermingled and the sample after secondary treatment has a difference to this according to the terms and conditions of the concentration of the ammonium hydrogendifluoride under bath, time amount, and temperature, as compared with the primary anodization back, it is white certainly, and it is thought that the low hypo---ic acid-ized titanium in a coat is removed from this by secondary treatment.

[0037] (Secondary anodic oxidation) The electrolysis time amount in secondary anodic oxidation, the condition of the coat by the concentration of ammonium hydrogendifluoride, and the photocatalyst activity of a coat are shown in Tables 1-3. These tables show that destruction of a coat takes place extremely for a short time, when secondary anodic oxidation is performed by the high-concentration bath. Moreover, it turns out that the coat stabilized when the concentration of ammonium hydrogendifluoride was not below 0.1M (M=mol/L) was not able to be obtained. As an overall trend, the good coat was obtained using the low-concentration bath by anodic oxidation in a short time for 10 minutes or for 5 minutes.

[0038]

[Table 1]

二次陽極酸化の条件による皮膜の状態と光触媒活性(浴温20℃)

NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)	NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)
0.01mol/l	5	○	0	0.3mol/l	5	×	
	10	○	2.4		10	×	
	15	○	2		15	×	
	30	×			30	×	
0.05mol/l	5	○	7.1	0.5mol/l	5	×	
	10	○	7.4		10	×	
	15	○	7.1		15	×	
	30	×			30	×	
0.1mol/l	5	○	10.2				
	10	×					
	15	×					
	30	×					

\* 電解条件は、150V、3.0A/dm<sup>2</sup>

分解能はアセトアルデヒドを封入した容器中に皮膜を入れ、これに可視光を照射したときのアセトアルデヒド分解量

皮膜の状態: ○ 皮膜に問題がない状態

△ 皮膜の形状自体には問題ないが表面に斑点などが生じた状態

× 皮膜がはがれた状態

[0039]

[Table 2]

二次陽極酸化の条件による皮膜の状態と光触媒活性(浴温30℃)

NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)	NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)
0.01mol/l	5	○	7.4	0.3mol/l	5	×	
	10	○	7.2		10	×	
	15	○	10		15	×	
	30	×			30	×	
0.05mol/l	5	○	15.7	0.5mol/l	5	×	
	10	○	17.6		10	×	
	15	△			15	×	
	30	×			30	×	
0.1mol/l	5	○	18				
	10	×					
	15	×					
	30	×					

\* 電解条件は、150V、3.0A/dm<sup>2</sup>

分解能はアセトアルデヒドを封入した容器中に皮膜を入れ、これに可視光を照射したときのアセトアルデヒド分解量

皮膜の状態: ○ 皮膜に問題がない状態

△ 皮膜の形状自体には問題ないが表面に斑点などが生じた状態

× 皮膜がはがれた状態

[0040]

[Table 3]

二次陽極酸化の条件による皮膜の状態と光触媒活性(浴温40℃)

NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)	NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)
0.01mol/l	5	○	5.4	0.3mol/l	5	×	
	10	○	8.9		10	×	
	15	○	6.5		15	×	
	30	×			30	×	
0.05mol/l	5	○	17.6	0.5mol/l	5	×	
	10	○	15.1		10	×	
	15	×			15	×	
	30	×			30	×	
0.1mol/l	5	×					
	10	×					
	15	×					
	30	×					

\* 電解条件は、150V、3.0A/dm<sup>2</sup>

分解能はアセトアルデヒドを封入した容器中に皮膜を入れ、これに可視光を照射したときのアセトアルデヒド分解量

皮膜の状態: ○ 皮膜に問題がない状態

△ 皮膜の形状自体には問題ないが表面に斑点などが生じた状態

× 皮膜がはがれた状態

[0041] Next, the condition of the coat at the time of being immersed in ammonium hydrogendifluoride is shown in Tables 4 and 5. These tables show that the coat which has photocatalyst activity is unproducible in the experiment by immersion.

[0042]

[Table 4]

浸漬実験による皮膜の状態(浴温20℃)

NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)	NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)
0.01mol/l	5	○	0	0.1mol/l	5	○	0
	10	○	0		10	○	0
	15	○	0		15	○	0
	30	○	0		30	×	
	45	○	0		45	×	
	60	○	0		60	×	
0.05mol/l	5	○	0	0.3mol/l	5	○	0
	10	○	0		10	○	0
	15	○	0		15	○	0
	30	○	0		30	×	
	45	○	0		45	×	
	60	×			60	×	

皮膜の状態: ○ 皮膜に問題がない状態

△ 皮膜の形状自体には問題ないが表面に斑点などが生じた状態

× 皮膜がはがれた状態

[0043]

[Table 5]

浸漬実験による皮膜の状態(浴温30℃)

NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)	NH <sub>4</sub> FHF濃度	電解時間	皮膜の状態	分解能(%)
0.01mol/l	5	○	0	0.1mol/l	5	○	0
	10	○	0		10	○	0
	15	○	0		15	×	
	30	○	0		30	×	
	45	○	0		45	×	
	60	×			60	×	
0.05mol/l	5	○	0	0.3mol/l	5	○	0
	10	○	0		10	○	0
	15	○	0		15	×	
	30	×			30	×	
	45	×			45	×	
	60	×			60	×	

皮膜の状態: ○ 皮膜に問題がない状態

△ 皮膜の形状自体には問題ないが表面に斑点などが生じた状態

× 皮膜がはがれた状態

[0044] (Photocatalyst activity) the acetaldehyde according to the light exposure of the sample after secondary anodization to drawing 1 -3 -- resolution is shown. Titanium plate 0.15dm<sup>2</sup> It is the neighboring amount of decomposition. As on the whole as about 10% at 20 degrees C of bath temperature, resolution is lower than drawing 1. Therefore, in this bath temperature, it is guessed that the solubility of low hypo---ic acid-ized titanium is small. The sample with the highest resolution is 5min in the solution containing the ammonium hydrogendifluoride of 0.1M, and the hydrogen peroxide of 1M. It is 10min in the solution which the coat has become quite weak as for this sample, and, on the whole, contains the ammonium hydrogendifluoride and the hydrogen peroxide of 0.05M although it is the anodized sample. Or 5min It turned out that the anodized sample is excellent. In addition, although the experiment of photocatalyst activity was conducted on the light source by light exposure using the xenon lamp, the cut-off filter which intercepts ultraviolet rays 400nm or less was attached before the light source at this time.

[0045] XRD measurement (X diffraction measurement)

A crystalline change of the coat by whenever [ bath temperature / at the time of primary anodic oxidation ] is shown in drawing 4. From this drawing, a rise of the temperature at the time of primary anodic oxidation checks that the peak of 25-degree C ANATASU is growing. However, if secondary treatment is performed to the coat which performed primary anodic oxidation in a bath (40 degrees C and 50 degrees C), the time amount by which a coat is destroyed compared with the sample processed below 30 degrees C will become early extremely. Therefore, whenever [ bath temperature / of primary anodizing ] was set up with 30 degrees C. Moreover, although not shown in drawing, as for change, after secondary anodic oxidation and immersion were not seen by the XRD pattern.

[0046] EPMA measurement (electronic PUROGU electron probe X-ray microanalyser measurement)

The result of the EPMA measurement after secondary anodic oxidation is shown in drawing 5 after primary anodic oxidation at drawing 6. Lynn of a considerable amount and sulfur with which titanium, and the phosphoric acid and sulfuric acid other than oxygen are considered to be the causes over the whole coat in both were checked from these drawings. It is thought that these anions were incorporated by the coat by electrical machinery migration. In addition, although a fluorine was not detected from the coat after secondary anodic oxidation, it is surmised that this is because concentration is low.

[0047] XPS measurement (X-ray-photoelectron-spectroscopy measurement)

When the depth direction analysis by XPS measurement was performed to the sample which performed the amount of secondary anodic oxidation, it was checked that the fluorine exists in a coat and it was checked that a fluorine is also incorporated by the coat by electrophoresis like phosphoric-acid ion or sulfur ion.

[0048] SEM image observation (scanning electron microscope image observation)

The SEM image after primary anodic oxidation and each secondary treatment is shown in drawing 7. It turns out that all coats are carrying out the same configuration from these SEM images.

[0049] [Consideration of an experimental result] From the above result, by anodizing by the ammonium-hydrogendifluoride bath as secondary treatment showed that photocatalyst activity could be given to an anodic oxide film. It is considered effective in removing the low hypo---ic acid-ized titanium in a coat, and coincidence by this to dope a fluorine in a coat. The sample of this of an immersion experiment is clearer than catalytic activity was not shown but the sample by secondary anodic oxidation showed catalytic activity. That is, at the time of secondary anodization, the fluorine ion of the ammonium hydrogendifluoride used for low hypo---ic acid-ized titanium removal enters into a titanium oxide coat by electrophoresis, and builds impurity level, and it is possible that photocatalyst activity improved as a result etc.

[0050] Next, it is in the coat which re-anodized the titanium anodic oxide film obtained in said examples 2-8, and the result of having examined the photocatalyst operation over the light is shown in Table 6. As shown in this table, it was checked by re-anodizing the titanium anodic oxidation coatings obtained in the examples 2-8 that an acetaldehyde can be decomposed by the light.

[0051]

[Table 6]

【表 6】

試料	死亡率 (%)
実用例 2 を再陽極酸化	7 4
実用例 3 を再陽極酸化	6 7
実用例 4 を再陽極酸化	6 0
実用例 5 を再陽極酸化	5 5
実用例 6 を再陽極酸化	4 9
実用例 7 を再陽極酸化	4 6
実用例 8 を再陽極酸化	4 4

※試料は 1.0dm<sup>2</sup> (10cm×10cm) に換算した。

[0052] in addition, the titanium anodic oxide film which performed each \*\*\*\*\* [ more than ] -- attaching -- the [ said ] -- the [ 1 another operation gestalt and ] -- the [ 2 another operation gestalt and ] - - when processing performed by either of the 3 another operation gestalten is performed, it is guessed that antibacterial [ much more desirable ], deodorization, and the antifouling effectiveness are acquired. For example, either of the degrees is processed. After generating the re-anodized titanium anodic oxide film, the removal process in which the sulfuric acid and phosphoric-acid ion in an anodic oxide film are removed is given by replacing an anode plate and cathode and electrolyzing by changing an electrical potential difference. The re-anodized titanium is immersed into the water solution of the chloride of noble metals, UV irradiation is performed, and the colloid deposit process in which the reduction deposit of the colloid of noble metals is carried out on the surface of an anodic oxide film is given. The titanium [ finishing / re-anodizing ] used as the object which performs these processings may be re-anodized by the above-mentioned this gentleman [ any ] method.

[0053]

[Effect of the Invention] As mentioned above, according to this invention, a photocatalyst operation can be demonstrated not only by ultraviolet rays but by the visible ray, and antibacterial [ outstanding ], deodorization, and the antifouling effectiveness can be acquired.

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[Translation done.]